



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 295 343
A1**

EUROPEAN PATENT APPLICATION

Application number: 87305335.9

Int. Cl.⁴ **C04B 38/00 , //B01J35/04,
F01N3/02,B01D46/10**

Date of filing: 16.06.87

Date of publication of application:
21.12.88 Bulletin 88/51

Designated Contracting States:
BE DE FR GB SE

Applicant: **NGK INSULATORS, LTD.**
2-56, Suda-cho, Mizuho-ku
Nagoya City Aichi Pref.(JP)

Inventor: **Otaka, Masashi**
778-2 Ohaza-Obuke
Asahi-cho Mie-gun Mie Pref(JP)
Inventor: **Asai, Showji**
59-1 Iwato-cho 4-chome Minami-ku
Nagoya City Aichi Pref(JP)

Representative: **Williams, Trevor John et al**
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5EU(GB)

Method for producing ceramic honeycomb structural body.

A method for producing a highly reliable ceramic honeycomb structural body having selectively, tightly sealed open end surfaces, which comprises steps of attaching a film or mask on an open end surface of a ceramic honeycomb structural body, introducing a ceramic sealing material preferably having a viscosity of 50-1,500 poises into throughholes of said honeycomb body through apertures bored at selected positions of the film or mask, and drying to solidify the sealing material followed by sintering, wherein particularly the drying is commenced with 2 minutes after the introduction of the sealing material into the throughholes and is rapidly performed, preferably with hot air at 100-300 °C.

EP 0 295 343 A1

METHOD FOR PRODUCING CERAMIC HONEYCOMB STRUCTURAL BODY

The present invention relates to a method for producing a ceramic honeycomb filter which is used for removing fine particles in diesel engine exhaust gas or for chemical industries, or a ceramic honeycomb structural body for heat exchangers. More particularly, this invention relates to a method for sealing open ends of throughholes of the ceramic honeycomb structural body.

Regarding a method for sealing open ends of throughholes of the ceramic honeycomb structural body, there is known a method which comprises steps of attaching a film or mask on an open end surface of a ceramic honeycomb structural body, and introducing a ceramic sealing material into throughholes of the ceramic honeycomb structural body through apertures provided at selected positions of the film or mask, to seal an end portion of the throughholes of the ceramic honeycomb structural body (US Patents Nos. 4,293,357 and 4,559,193).

In US Patent No. 4,293,357, as the ceramic sealing materials, those having dilatancy are used, and US Patent No. 4,559,193 discloses a method comprising steps of dipping a honeycomb body in a slurry containing a sealing material and passing a pasty sealing material green body into throughholes of the honeycomb body.

However, the use, as the sealing material, of a dilatant sealing material has drawbacks in that a tight sealing cannot be provided between partition walls defining the throughholes and the sealing material, because of a smaller diameter of apertures bored through the film as compared with the diameter of the throughholes of the ceramic honeycomb structural body, or the sealing material bridging the apertures of the film due to the dilatancy, which hinders a smooth introduction of the sealing material into the throughholes.

It is more effective for ensuring a tight sealing between partition walls and sealing layer to use a viscous slurry. However, the use of such a slurry has drawbacks in that an open pore is prone to be formed in the center portion of the sealing layer. In particular, for sealing of a porous ceramic honeycomb structural body, the drawbacks become more conspicuous because the sealing material penetrates through the pores of the porous ceramic body to draw the sealing layer towards the partition walls.

Therefore, the use of two phases of sealing materials, i.e., a viscous material and a dilatant material, has been proposed to ensure a tight sealing without forming the central hole. However, the use of two phases of sealing material requires two sealing steps, which is not suitable for mass production.

The present invention is aimed to eliminate the above-mentioned drawbacks of the prior art.

The object of the present invention is to provide a method for sealing, with a high reliability, an end portion of throughholes of a porous ceramic honeycomb structural body.

The above object can be attained by a method for producing a ceramic honeycomb structural body having selectively sealed open end surfaces, which method comprises steps of attaching a film or mask on an open end surface of a ceramic honeycomb structural body and introducing a ceramic sealing material into throughholes of the ceramic honeycomb structural body through apertures provided at selected positions of the film or mask, which is characterized in that drying of the sealing material is commenced within 2 minutes after the introduction of said sealing material into the throughholes and completed with solidification of the sealing material.

For a better understanding of the invention, reference is made to the accompanying drawing, in which:

Fig. 1 is a flow sheet for illustrating the method of the present invention.

Referring to Fig. 1, in the first step, a ceramic honeycomb structural body is prepared. As a material for the ceramic honeycomb structural body, those having heat resistance, thermal shock resistance, etc., such as cordierite, alumina, mullite and the like, are selected depending on the use. Further, the form of the throughholes and the size and shape of the whole honeycomb body are generally decided also depending on the use. Since ceramic honeycomb structural bodies to which the method of the present invention is applied are mainly used as ceramic filters, etc., those having a throughhole density (the number of cells per cross-sectional unit area) of 2-100/cm² are preferred in view of characteristics required for filters, such as filtration area and pressure loss.

As the preparation process, an extrusion molding is generally adopted and then a fired product or a greenware is prepared.

The next step is a step of attaching a film on an opening surface of the ceramic honeycomb structural body. As the film, use may be made of either a film having apertures bored in advance at selected positions corresponding to desired throughholes to be sealed at an end portion with a sealing material, or a film having apertures bored at selected positions after the film has been attached. Additionally, in this step, not only the film but also a rubber mask having apertures bored in advance, may be used.

The following step is a most important step in the practice of the present invention, wherein the ceramic sealing material is introduced into selected throughholes through the apertures.

As a main ingredient of the sealing material, the same material as that of the ceramic honeycomb structural body is preferably used, that is, for example, cordierite, alumina, mullite, etc. Other than these main ingredients, it contains a plasticizer, such as a binder, water, etc. As the binder, those rapidly solidifiable upon heating, such as methyl cellulose, polyvinyl alcohol, carboxymethyl cellulose, starch paste, polyethylene oxide, etc., are preferred, in order to rapidly dry the sealing material, as will be described hereinafter.

For example, when sealing material compositions of cordierite system are used, 100 parts by weight of cordierite powder or a mass formulated with predetermined raw materials such that after being fired the mass has substantially the same composition as the cordierite system, are admixed with a binder consisting of 0.2-5.0 parts by weight of methyl cellulose, 5-15 parts by weight of glycerine and 0.1-2 parts by weight of polyethylene oxide, and are further added and kneaded with 25-40 parts by weight of water as a plasticizer, and then the viscosity of the resultant is adjusted to a predetermined value to prepare a sealing material. The viscosity of the sealing material is selected depending on the throughhole size of the ceramic honeycomb structural body to be sealed. For example, by the throughhole density being 2 cells/cm², it is meant that the throughholes are of relatively large size, such as having a polygonal cross-section with a side length of about 7 mm or a circular cross-section of about 7 mm in diameter. In this case, even a relatively high viscosity can be selected for the sealing material. However, when the viscosity is too low, there may be the case where a single step fails to seal. In that case, the sealing can be achieved by repeating the steps of the introduction of the sealing material and the subsequent drying and solidification.

On the other hand, by the throughhole density being, for example, 200 cells/cm², it is meant that the throughholes are of small size, such as having a polygonal cross section with a side length of about 1 mm or a circular cross-section of about 1 mm in diameter. In this case, a relatively low viscosity is selected.

In the present invention, it is preferred that the viscosity of the sealing material is adjusted to be 50-1,500 poises, preferably 100-800 poises.

The reason why the above limited viscosity range is preferred is that, in the case of lower than 50 poises, a small hole tends to grow in the central portion of the seal at an end of the throughhole, though a good tightness is attained between the sealing material and the partition walls of the ceramic honeycomb structural body, while, if in excess of 1,500 poises, the tightness will be poor between the sealing material and the partition walls, and particularly when the throughholes have a square cross-section, the corners will not be able to be sealed tightly. The viscosity is adjusted with the viscosity and amount of main ingredients, the kind and amount of the binders, and a solvent such as water or the like.

As a means for introducing the ceramic sealing material into the throughholes, pressing, dipping, etc. are adopted. The introduction may be effected into each open end surface alternately or both the surfaces simultaneously.

The subsequent step is a step of drying the sealing material introduced into the throughholes.

The sealing material is dried immediately after the introduction thereof into the throughholes. The drying should be commenced within 2 minutes after the introduction of the sealing material.

The reason for the above is, when a porous ceramic honeycomb structural body is sealed, the sealing material tends to be more absorbed into the partition walls and the seal is not formed in the central portion and a small hole tends to be formed in the central portion. The tendency of the above drawbacks becomes remarkable, particularly when the viscosity is low. Therefore, sealing material must be dried and solidified in a short time after the introduction into the throughholes, before the sealing material is excessively absorbed into the pores of the porous ceramic honeycomb structural body. For example, when the viscosity is, for instance, 100-300 poises, the time from the pressing-in to the drying is preferably within 1 minute, more preferably within 30 seconds. The drying means is adequately selected in accordance with the properties of the sealing material, and a heating means such as hot air and gas burner, and an electric heating means such as nichrome heater, infra-red ray heater, and the like, may be adopted. As the drying temperature, a temperature of 100-300°C is preferred. This is because, when lower than 100°C, the drying is so insufficient that the sealing material may exfoliate by handling in the next step, or even if not exfoliates, a drawback will be encountered such that the drying time is prolonged. Further, if higher than 300°C, the binders, etc. contained in the sealing material will be eliminated so that an adhering strength of the sealing material to the throughholes is prone to decrease. Furthermore, when the ceramic honeycomb structural body is a greenware, i.e., a non-fired product, the elimination of the binders contained in the honeycomb structural body causes deterioration in strength of the honeycomb structural body, whereby cracking and chipping become liable to occur.

The drying time is selected so as to be sufficient for the sealed portion to solidify. It is set depending

on the shape of the product, the drying temperature, the viscosity of the sealing material, etc., and generally 0.5-3 minutes.

The final step is a step of sintering the sealing material. When the ceramic honeycomb structural body is a sintered body, sintering conditions are determined depending on the main ingredient of the sealing material. For example, in the case of a cordierite system, sintering at 1,400°C for 4 hours is preferred. On the other hand, when the ceramic honeycomb structural body is a greenware, the conditions are determined, taking the material, size and shape of the ceramic honeycomb structural body into account.

The following example is given for the purpose of illustration of this invention and is not intended as limitations thereof.

Example

As ceramic honeycomb structural bodies, three kinds shown in Table 1 were prepared. Then, the throughholes of the ceramic honeycomb structural bodies were sealed at an opening end with sealing materials shown in Table 2, under conditions shown in Table 3.

Of the thus obtained ceramic honeycomb structural bodies having throughholes sealed at an opening end, the sealed portions were checked with the naked eye by the aid of a light projector. The results are given in Table 4. As is apparent from those results, the sealed bodies produced by the method of the present invention are excellent.

Table 1

No.	Material	State of Product	Dimension and Shape of Ceramic Honeycomb Body				
			Dia. (mm)	Height (mm)	Wall Thickness (mm)	No. of cells (No./cm ²)	Cross-section of cell
A	Cordierite	Fired	144	150	0.4	15.5	Square
B	Mullite	Fired	120	150	0.3	31.0	Square
C	Cordierite	Green	120	150	0.4	15.5	Square

Table 2

(Unit: weight %)

Composition	Main Ingredient	Methylcellulose	Polyethylene oxide	Polyvinyl alcohol	Carboxymethyl cellulose	Glycerine	Water reducing agent	Water
a	Cordierite	0.5	0.2	-	-	10	0.3	18~32
b	Mullite	1.0	-	5.0	-	-	-	40
c	Cordierite	0.5	-	-	3.0	-	-	40

Table 3(a)

No.	Ceramic honeycomb structural body	Sealing material		Seal- ing Means	Time from pressing-in to commencement of drying of sealing material (sec.)	Conditions for drying			Conditions for firing	
		Compo- sition	Vis- cosity (P)			Time (sec.)	Means	Temp. (°C)	Temp. (°C)	Time (hr)
1	B	b	50	Film	15	60	Electric heater	250	1420	6
2	C	c	50	Mask	30	60	Hot air	300	1410	2
3	A	c	50	Mask	120	60	Hot air	400	1410	2
4	B	a	100	Film	120	60	Electric heater	250	1420	6
5	A	a	250	Mask	30	180	Hot air	80	1400	4
6	A	a	250	Mask	120	180	Hot air	80	1400	4
7	A	a	250	Mask	90	120	Hot air	100	1400	4
8	A	a	250	Mask	60	90	Hot air	200	1400	4
9	C	c	250	Mask	30	60	Hot air	300	1410	2
10	B	b	300	Film	15	60	Electric heater	250	1420	6
11	B	b	300	Film	30	60	Electric heater	250	1420	6
12	B	b	300	Film	60	60	Electric heater	250	1420	6
13	B	b	300	Film	120	60	Electric heater	250	1420	6
17	B	b	300	Film	240	60	Electric heater	250	1420	6

Table 3(b)

No.	Ceramic honeycomb structural body	Sealing material		Sealing Means	Time from pressing-in to commencement of drying of sealing material (sec.)	Conditions for drying			Conditions for firing	
		Composition	Viscosity (P)			Time (sec.)	Means	Temp. (°C)	Temp. (°C)	Time (hr)
14	B	b	600	Film	30	60	Electric heater	250	1420	6
15	A	a	1500	Mask	90	120	Hot air	100	1400	4
18	B	b	1500	Film	240	60	Electric heater	250	1420	6
16	C	c	1500	Mask	30	60	Hot air	300	1410	2
19	A	a	30	Mask	30	120	Hot air	80	1400	4
20	B	b	30	Film	60	60	Electric heater	250	1420	6
21	C	c	30	Mask	30	60	Hot air	300	1410	2
22	C	c	30	Mask	15	60	Hot air	400	1410	2
23	A	a	2200	Mask	120	120	Hot air	80	1410	2
24	C	c	2200	Mask	120	60	Hot air	400	1410	2

Notes) 1) Nos. 17-24 are reference examples.

2) Hot air: Air was heated with a nichrome heater and the hot air was passed to sealed surfaces.

3) Electric heater: The sealed surface was placed to face to ignited surfaces of a nichrome heater and temperatures of the sealed surface and nichrome heater were set to predetermined values.

Table 4

No.	Sealed conditions	Result of checking
1	No defect observed.	◎
2	No defect observed	◎
3	No defect observed.	○
4	No defect observed.	◎
5	No defect observed.	○
6	No defect observed.	○
7	No defect observed.	◎
8	No defect observed.	◎
9	No defect observed.	◎
10	No defect observed.	◎
11	No defect observed.	◎
12	No defect observed.	◎
13	No defect observed.	◎
14	No defect observed.	◎
15	No defect observed.	◎
16	No defect observed.	◎
17	A small hole in every sealed portion.	x
18	A small hole in every sealed portion.	x
19	A small hole in every sealed portion.	x
20	A small hole in every sealed portion.	x
21	A small hole in every sealed portion.	x
22	A small hole at the center of seal, and cracks in honeycomb.	x
23	Gaps in corners of seal.	x
24	Gaps in corners of seal, and cracks in honeycomb.	x

Notes) 1) Nos. 17-24 are reference examples.
 2) Evaluation: ◎; Excellent
 ○; Good
 x; No good

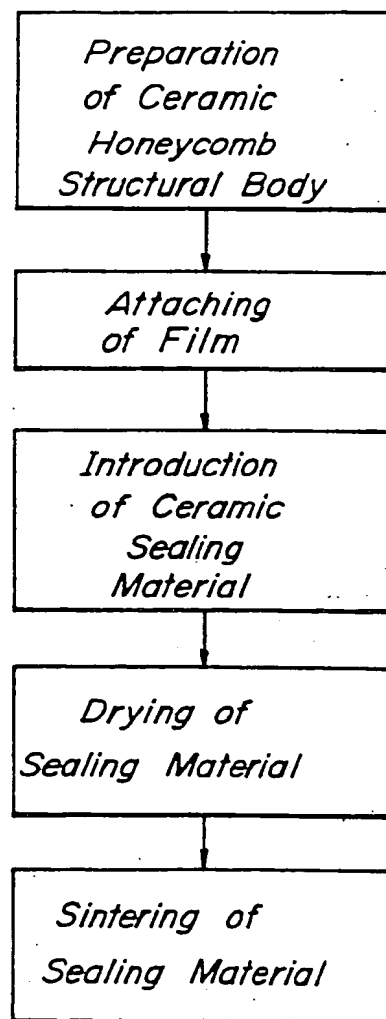
As seen from the above explanation, by the method according to the present invention, drying of the sealing material is commenced immediately after introduction thereof into throughholes of honeycomb bodies, so that highly reliable ceramic filters are obtainable with a simple operation.

Claims

1. A method of producing a ceramic honeycomb structural body having selectively sealed open end surfaces, comprising steps of attaching a film or mask on an open end surface of a ceramic honeycomb structural body and introducing a ceramic sealing material into throughholes of the ceramic honeycomb structural body through apertures provided at selected positions of the film or mask, characterised in that the sealing material has a viscosity of 50 to 1500 poises, drying of the sealing material being commenced within two minutes after the introduction of said sealing material into the throughholes and completed with solidification of the sealing material.

2. A method as claimed in claim 1, characterised in that the drying is performed by passing hot air at a temperature of 100 to 300 °C for 0.5 to 3.0 minutes.

FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 30 5335

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, A	EP-A-0 042 302 (NGK INSULATORS) -----		C 04 B 38/00 // B 01 J 35/04 F 01 N 3/02 B 01 D 46/10
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 04 B 38/00 C 04 B 41/00 B 01 J B 01 D F 01 N 3/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-02-1988	Examiner DAELEMEN P.C.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			